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^{35}Cl, ^{81}Br AND ^{127}I NQR SPECTRA OF CYCLOPENTADIENYLTITANIUM HALIDES

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Summary

NQR spectra of ^{35}Cl, ^{81}Br and ^{127}I in cyclopentadienyltitanium halides Cp_nTiHal_{4-n} have been studied. Quadrupole coupling constants of the halogen atoms regularly increase with the increasing number of Cp rings in the molecule, which is apparently connected with the decreasing multiplicity of the Ti—Hal bond. A sharp increase in the asymmetry parameters of the iodine atom on introduction of the Cp rings is evidence for an essential desymmetrization of the electron density in the molecule caused by this operation.

Introduction

A number of papers in which the properties of the titanium—halogen bond in titanium tetrahalides and cyclopentadienyltitanium halides are discussed have appeared in recent years.

To elucidate the nature of the Ti—Hal bond we have undertaken a detailed study of NQR spectra of chlorine, bromine and iodine in cyclopentadienyltitanium halides.

Experimental

NQR spectra of titanium derivatives were recorded on a pulse NQR spectrometer. The data obtained are listed in Table 1.

Cyclopentadienyltitanium derivatives were synthesized according to published procedures [1—4], their characteristics were identical with those reported in the literature.

TABLE 1

^{35}Cl, ^{81}Br, ^{127}I NQR SPECTRA OF CYCLOPENTADIENYLTITANIUM HALIDES AT 77 K

Compound	^{35}Cl		^{81}Br		^{127}I					
	ν (MHz)	S/N	ν (MHz)	S/N	$\nu(1/2-3/2)$ (MHz)	S/N	$\nu(3/2-5/2)$ (MHz)	S/N	e^2Qq (MHz)	η (%)
$TiHal_4$ [a]	5.9802 [d]		39.214 [f,g]	20						
	6.0380		39.368	20						
	6.0807		39 656	20						
	6.1118		40.089	20						
			38.679	20	43.650	5	87.298	10	291.0	0
			39.361	60	44.890	15	89.780	30	299.2	0
$C_5H_5TiHal_3$ [b]	8.042 [e]	6	55.12 [f]	15	88.822	10	125.010	10	442.6	60.5
	8.145	3	55.31	15	88.498	10	124.764	10	441.6	60.3
			55.74	15	86.012	10	118.474	10	421.2	62.9
$(C_5H_5)_2TiHal_2$ [c]	11.764 [e]	5	80 430 [f]	10	128 400	10	198 070	5	689.8	44.9
	11.884	5	81.494	10	126.150	4	195.300	2	679.6	49.5
	12.028	5	81.690	10						
	12.208	5	83.580	10						

[a] The spectrum of one of the studied TiI_4 specimens consisted of four lines of frequencies of 68.95, 82.69 96.12 and 145.10 MHz If the 68.95 and 82.69 MHz frequencies are assigned to the transition 1/2—3/2 and two others to the transition 3/2—5/2, e^2Qq_{zz} and η would be 301.8 (η = 78.5) and 507.2 MHz (η = 52.5%) respectively. If 68.95 and 82.69 MHz frequencies correspond to the transition 1/2—3/2, then e^2Qq_{zz} values are 340.9 (η = 61 6) and 494 1 MHz (η = 33 5%). Large asymmetry parameters of iodine atoms can be ascribed to strong intermolecular association interactions Ti I arising in this phase of TiI_4. [b] A strong "piezoeffect" was observed. [c] e^2Qq_{zz} = 679.6 MHz, η = 49.5%, $\nu(1/2-3/2)$ = 126 15 and $\nu(3/2-5/2)$ = 195.30 MHz at 295 K. [d] Ref. 18. [e] Ref. 9. [f] Ref. 8. [g] Ref. 20.

Results and discussion

According to PMR data for bis(cyclopentadienyl)titanium halides the electron density on nuclear protons increases in the series I < Br < Cl < F in spite of the increasing electronegativity of the halogen atoms [5-7]. NQR spectra of titanium bromides [8] and chlorides [9] show an increase in the quadrupole coupling constants of the halogen atoms with the increasing number of electron-donor groups. NMR frequencies of ^{19}F for bis(cyclopentadienyl)titanium difluorides lie in a very weak field; chemical shift values of ^{19}F in nitrobenzene are: -156.4 for $(C_5H_5)_2TiF_2$, -153.9 for $(CH_3C_5H_4)_2TiF_2$ and -145.0 ppm for $[(CH_3)_5C_5]C_5H_5TiF_2$ [7].

The regularities found in all cited works [7] were explained by a possible resonance interaction of lone pairs of the halogen atoms with the vacant orbitals of the titanium atom. The data obtained after a careful comparison of the (*M*—Hal) and (*M*—C_oH_5) peak intensities by means of a detailed mass spectrometry study of bis(cyclopentadienyl) halides and cyclopentadienyl trihalides do not contradict the conclusion about an increase of the bond multiplicity in the series I < Br < Cl < F [10]. NQR frequencies of ^{35}Cl and ^{79}Br are essentially lower than would be expected if one takes into account the electronegativity of titanium which according to Lucken's estimation [11] corresponds to 30% double bond character of the Ti—Hal bond. Additionally, in the NQR spectrum of $TiBr_4$ an abnormally low value of Stark-splitting (a frequency shift caused by a constant external electric field) ~ 200 Hz has been found [12]. It has been shown [11] that the application of an external electric field leads to a change in NQR frequencies caused by the influence of this field on π- and σ-electrons of a resonant halogen atom, the contributions of π- and σ-electrons having opposite signs [terms $(N_x + N_y)/2$ and N_z in the Townes and Dailey formula, respectively*].

Thus, the participation of π-electrons in additional bondings has to cause a general decrease in Stark-shift of the NQR frequency. If there is no π-bonding, p_π-electron density of a halogen atom is constant and a Stark-shift which is only due to the polarization of a σ-bond is much more significant.

For cyclopentadienyltitanium halides and alkoxytitanium halides we found that NQR frequencies of ^{35}Cl, ^{81}Br, ^{127}I in the series $(C_5H_5)_nTiHal_{4-n}$ (n = 0-2; Hal = Cl [9], Br [8], and I) increase sharply with the increasing n. In the series $C_5H_5Ti(OC_2H_5)_nBr_{3-n}$ (n = 1-3), the same occurs with the increasing number of ethoxy groups in the molecule [8]. At the same time, a characteristic feature of the halogen derivatives of Group IVB is an increase in NQR frequencies on introducing electron-acceptors in the molecule, and a decrease in NQR frequencies if electron-donor substituents are introduced; this is principally caused by a change in the ionicity of the M—Hal bond. The increase in halogen frequencies in the series $TiHal_4 < CpTiHal_3 < (Cp)_2TiHal_2$ is monotonous. As it is seen from Fig. 1 the dependence of the number of unbalanced p-electrons U_p on the number of Cp rings in the molecule is nearly the same for chlorine, bromine and iodine atoms. A certain increase in the U_p value in the series Cl < Br < I might be connected

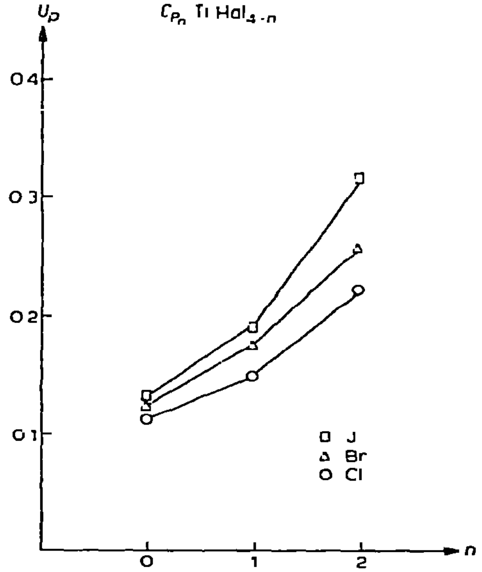

Fig. 1. The relationship between the number of unbalanced p electrons (U_p) and the number of the cyclopentadienyl rings (n) in a Cp_nTiHal_{4-n} molecule.

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* According to the semi-empirical Townes and Dailey [19] relationship the number of unbalanced p-electrons (U_p) by which the electric field gradient at the nucleus of a halogen atom is determined, is defined by the formula $U_p = (N_x + N_y)/2 - N_z$, where N_x, N_y and N_z are the populations of p_x, p_y and p_z halogen orbitals, p_z orbitals taking part in forming δ-bond while p_x and p_z orbitals may contribute to π-bonding.

with an increase in the polarization of the core of the halogen atom when passi from chlorine to iodine. If one assumes the validity of the Townes and Dailey relationship for titanium derivatives, and the fact that a Cp ring is a more effective π-donor than a halogen atom, then an increase in the number of π-donor substituents will lead to a decrease in the drawing of electron density from p_x and p_y halogen orbitals to the vacant titanium orbitals. The latter will increase the populations of N_x, N_y of these orbitals causing, in accordance with ref.10, a increase in NQR frequencies. The increase in NQR frequencies for cyclopentadienylalkoxytitanium bromides [8] with the increasing number of ethoxy group whose π-donor properties are well known, can be also explained from the viewpoint quoted above.

An increase in NQR frequency caused by the introduction of Cp ligands in a $TiHal_4$ molecule is followed by a change in the Ti—Cl bond length in the series of corresponding compounds, which according to X-ray investigations increases in the series $(C_5H_5)_nTiCl_{4-n}$ ($n = 0$-2) as follows: $TiCl_4$ (2.18) < $C_5H_5TiCl_3$ (2.29) < $(C_5H_5)_2TiCl_2$ (2.36 Å) [13-15].

It is interesting to note that besides an increase of halogen NQR frequency with the increasing number of Cp rings or ethoxy groups in the $TiCl_4$ molecule, there also occurs a pronounced decrease in the mobility of halogen atoms entering nucleophilic substitution reactions [8]. For example, $TiCl_4$ is known to react with an excess of alcohol to form $(RO)_2TiCl_2 \cdot ROH$; in the reaction of $(RO)_3TiCl$ with alcohols only a reesterification occurs. To obtain titanium tetraalkoxyhalides starting from titanium tetrahalides and alkoxytitanium halides one has to use HHal acceptors. In the reactions of $CpTiHal_3$ with alcohols only one halogen atom is substituted and in spite of harder reaction conditions the yield of $CpTi(OR)Hal_2$ drops sharply if the cyclopentadienyl ligand bears electron-donor substituents. It should be also noted that the substitution of one halogen atom in $CpTiCl_3$ by a cyclopentadienyl strongly affects the mobility of chlorine in the reaction with alcohol. It decreases to such extent that no chlorine is replaced by an alkoxy group even after boiling the alcohol solution of $(Cp)_2TiCl_2$ for 3 h.

Asymmetry parameters for halogen atoms in $TiBr_4$ [11] and TiI_4 are close to zero, which corresponds to the equal participation of both halogen p-orbitals in the bondings involving vacant titanium orbitals.

On the other hand, asymmetry parameters found in cyclopentadienyltitanium iodides are very large ($\approx$ 50-60%). It is hard to believe that these high values are due to internal strains in the molecule or to intermolecular associative forces since, as shown by X-ray studies of these compounds, there are no significantly shortened intra- or inter-molecular distances in their crystal structures [13-17]. However, X-ray analysis of $CpTiI_3$ and $(Cp)_2TiI_2$ has not been carried out as yet.

It is possible to assume that the introduction of Cp rings in $TiHal_4$ molecules leads to an extremely high asymmetry in the electron distribution on the central titanium atom. In the framework of the semi-empiric Townes—Dailey theory [10,11] it might result in essentially unequal contributions of two halogen p_π-orbitals to the Ti—Hal bond.

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